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## The $(\text{SO}_2)_2\text{N}_3^-$ Anion

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**Abstract:** The recently proposed  $(\text{SO}_2)_2\text{N}_3^-$  anion was structurally characterized by single crystal X-ray diffraction of the  $[\text{Cs}][(\text{SO}_2)_2\text{N}_3]$  salt ( $P2_1/c$ ,  $a = 8.945(2)$  Å,  $b = 10.454(2)$  Å,  $c = 8.152(2)$  Å,  $\beta = 109.166(3)^\circ$ ,  $Z = 4$ , and  $R_1 = 0.0329$  at 130 K). In the  $(\text{SO}_2)_2\text{N}_3^-$  anion, both  $\text{SO}_2$  ligands are coordinated to one terminal nitrogen atom of the  $\text{N}_3^-$  anion.

### Introduction

Sulfur dioxide has been extensively used as a non-aqueous inorganic solvent.<sup>1-3</sup> Many  $\text{SO}_2$  solvates of metal cations have been structurally well characterized by X-ray crystallography.<sup>4</sup> Halide and pseudo-halide anions, such as  $\text{F}^-$ ,<sup>5,6</sup>  $\text{Cl}^-$ ,<sup>6,7</sup>  $\text{Br}^-$ ,<sup>6</sup>  $\text{I}^-$ ,<sup>6,8</sup>  $\text{CN}^-$ ,<sup>9</sup>  $\text{SCN}^-$ ,<sup>10</sup>  $\text{OCN}^-$ ,<sup>11</sup> and recently  $\text{N}_3^-$ ,<sup>11,12</sup> were found to form adducts with  $\text{SO}_2$  in a 1:1 ratio. These adducts can be viewed as halosulfites and pseudohalosulfites. The strength of the bond between the anions and  $\text{SO}_2$  was found to decrease with increasing anion size.<sup>6,11,13</sup> In the  $\text{SO}_2\text{F}^-$  anion, the S-F bond is basically a single bond, while the S-anion bonds in  $\text{SO}_2\text{I}^-$  and  $\text{SO}_2\text{SCN}^-$  are best described as contacts or secondary bonds. In a recent paper in this journal, we reported the

synthesis of  $[M][SO_2N_3]$  and  $[M][(SO_2)_2N_3]$ ,  $M = N(CH_3)_4$  and Cs and their characterization by NMR and vibrational spectroscopy.<sup>12</sup> The  $[M][(SO_2)_2N_3]$  salts represent the first spectroscopically characterized adduct of  $SO_2$  with an anion in a 2:1 ratio in the solid state.<sup>12</sup> Vibrational spectroscopy of  $N_3^-$  in  $SO_2$  solution indicates the presence of the  $(SO_2)_2N_3^-$  anion.<sup>12</sup> In 1938, Jander and Mesech have studied the interaction of  $SO_2$  with the halide and  $SCN^-$  anions by vapor pressure measurements. They found evidence for the existence of 1:2, 2:1, 3:1, and 4:1 adducts, depending on the nature of the anion and counter-cation. However, no structural information was obtained.<sup>14</sup> A UV and infrared spectroscopic study of halides and halosulfites in  $SO_2$  solution provided evidence for the presence of 2:1 adducts. The structure proposed for the  $(SO_2)_2X^-$  anion involved an  $O_2S-SO_2$  moiety, coordinated to the halide through only one sulfur atom.<sup>6</sup>

In the present paper, we report the X-ray crystal structure of  $[Cs][(SO_2)_2N_3]$ , thereby establishing the structure of the  $(SO_2)_2N_3^-$  anion.

## Experimental Section

**Caution!** Azides are highly endothermic and often can decompose explosively. Although no explosion has occurred while conducting these experiments, they should be handled on a small scale with appropriate safety precautions.

**Materials and Apparatus.** Reactions were carried out in Teflon-FEP ampoules that were closed by stainless steel valves. Volatile materials were handled on a Pyrex glass vacuum line equipped with grease-free Kontes glass-Teflon valves. Nonvolatile solids were handled in the dry argon atmosphere of a glove box. The  $CsN_3$  was prepared by literature methods.<sup>15</sup> The  $SO_2$  (Air Products, anhydrous grade, 99.9%) was dried over  $CaH_2$ .

**Crystal Growth of  $[\text{Cs}][(\text{SO}_2)_2\text{N}_3]$ .** Inside the dry box, approximately 0.02g of  $\text{CsN}_3$  (0.07 mmol) was loaded into a 9-mm FEP tube, which was sealed on one side and fused to a piece of 3/8" FEP tubing equipped with a Whitey SS-IRF2 valve on the other side. Anhydrous  $\text{SO}_2$  (0.5 mL) was added in vacuo to the solid at  $-196^\circ\text{C}$ . After warming to room temperature to dissolve all the  $\text{CsN}_3$ , the tube was cooled to  $-64^\circ\text{C}$ , and the  $\text{SO}_2$  solvent was removed slowly under a dynamic vacuum at  $-64^\circ\text{C}$ , yielding a pale yellow crystalline solid. The ampoule was cut open at  $-78^\circ\text{C}$  under a dry nitrogen stream, and the crystals were immediately transferred into an aluminum trough, kept at  $-100^\circ\text{C}$  by a stream of cold dry nitrogen. A crystal selected in the cold stream was mounted on a glass fiber by rapidly bringing it into contact with a droplet of Fomblin oil (Z-25) adhering to the tip of the fiber. The mounted crystal was rapidly transferred into the cold nitrogen stream of the goniometer head. The crystal used in this study had the dimensions  $0.80 \times 0.34 \times 0.313 \text{ mm}^3$ .

**Crystal Structure Determination of  $[\text{Cs}][(\text{SO}_2)_2\text{N}_3]$ . (a) Collection and Reduction of X-ray Data.** X-ray diffraction data were collected using a Bruker 3-circle platform diffractometer, equipped with a SMART APEX CCD (charge coupled device) detector with the  $\chi$ -axis fixed at  $54.74^\circ$  (using the program SMART<sup>16</sup>), and using  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) from a fine-focus tube. The diffractometer was equipped with a cryo-cooler from CRYO Industries for low-temperature data collection using controlled liquid nitrogen boil off. Cell constants were determined from 60 ten-second frames at 130 K. A complete hemisphere of data was collected up to a resolution of  $0.75 \text{ \AA}$ . Processing was carried out by using the program SAINT,<sup>17</sup> which applied Lorentz and polarization correction to three-dimensionally integrated diffraction spots. The program SADABS<sup>18</sup> was used for the scaling of diffraction data, the

application of a decay correction, and an empirical absorption correction based on redundant reflections.

**(b) Solution and Refinement of the Structure.** All data were processed using the SHELXTL package (version 5.1)<sup>19</sup> for structure determination, refinement, and molecular graphics. The XPREP program was used to confirm the unit cell dimensions and the crystal lattices. The structure was solved by the direct method. Successive difference Fourier synthesis revealed all atoms. The structure was refined by the least squares method on  $F^2$ . All atoms were refined anisotropically. For the anisotropic displacement parameters, the  $U(eq)$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

## Results and Discussion

**Preparation and Crystal Growth of  $[Cs][(SO_2)_2N_3]$ .** Yellow 2:1 adducts of  $SO_2$  and either  $CsN_3$  or  $[N(CH_3)_4][N_3]$  precipitate from their  $SO_2$  solutions at low temperature.<sup>12</sup> While the  $[N(CH_3)_4][(SO_2)_2N_3]$  salt is only marginally stable in a dynamic vacuum at  $-64\text{ }^\circ\text{C}$ , *i. e.*, close to the freezing point of the  $SO_2$  solvent, the corresponding  $Cs^+$  salt is stable in a dynamic vacuum up to  $-30\text{ }^\circ\text{C}$ .

**Crystal Structure of  $[Cs][(SO_2)_2N_3]$ .** Details of the crystal data for  $[Cs][(SO_2)_2N_3]$  are provided in Table 1; the observed bond lengths, angles, and contacts are listed in Table 2, together with the geometric parameters previously calculated<sup>12</sup> for the  $(SO_2)_2N_3^-$  anion. The atomic coordinates and equivalent isotropic displacement parameters are listed in Table 3.

The  $[Cs][(SO_2)_2N_3]$  salt crystallizes in the monoclinic space group  $P2_1/c$  and contains the  $(SO_2)_2N_3^-$  anion (Fig. 1). The  $(SO_2)_2N_3^-$  anions form in double-layered sheets in the  $bc$ -plane, with half of the  $SO_2$  groups in the center and the azide groups on the perimeters of the sheets

(Fig. 2). The  $\text{Cs}^+$  cations are located within the sheets close to the perimeters and form contacts to the terminal azide nitrogen of the adjacent double-layers.

In the  $(\text{SO}_2)_2\text{N}_3^-$  anion, the two  $\text{SO}_2$  groups are bound to the same terminal nitrogen atom of  $\text{N}_3^-$ . The azide group is essentially linear with a significant difference in the N-N bond lengths (1.141(6) and 1.219(6) Å), which are very similar to those found in  $[\text{N}(\text{CH}_3)_4][\text{SO}_2\text{N}_3]$  (1.144(2) and 1.214(2) Å).<sup>11</sup> In the  $(\text{SO}_2)_2\text{N}_3^-$  anion, one S-N bond (2.201(5) Å) is significantly shorter than the second one (2.427(4) Å). However, both S-N bonds are longer than that found for the  $\text{SO}_2\text{N}_3^-$  anion in  $[\text{N}(\text{CH}_3)_4][\text{SO}_2\text{N}_3]$  (2.005(2) Å).<sup>11</sup> The marked difference between the S-N bond lengths observed for the two  $\text{SO}_2$  ligands in  $(\text{SO}_2)_2\text{N}_3^-$  is in contrast to the calculated structure of the free gaseous anion, in which both  $\text{SO}_2$  ligands exhibit similar S-N distances. The differences between the observed solid state and the calculated gas-phase structures are likely due to packing effects and anion-cation interactions in the solid state. The  $\text{Cs}^+$  cation forms strong interionic contacts to N(1), N(3) and the oxygen atoms of the anion which are as short as 3.114(3) Å (Fig. 3). Because of the weakness of the N-S bonds, the orientation of the  $\text{SO}_2$  groups in the  $(\text{SO}_2)_2\text{N}_3^-$  anion is largely governed by the contacts to the  $\text{Cs}^+$  cations. The agreement between the calculated and observed structures of the  $(\text{SO}_2)_2\text{N}_3^-$  anion is quite good considering the weak S-N bonds and the strong anion-cation interactions.

The observed structure of the 1,1- $(\text{SO}_2)_2\text{N}_3^-$  anion is in agreement with the previous predictions<sup>12</sup> which were based on the experimental vibrational spectra of the  $\text{Cs}^+$  and  $\text{N}(\text{CH}_3)_4^+$  salts. The 1,1-isomer has been calculated to be more stable than the 1,3- $(\text{SO}_2)_2\text{N}_3^-$  anion by 3.5 (0.4) kcal/mol at the B3LYP (MP2) level of theory.<sup>12</sup> Preferential 1,1-coordination has also been observed for the  $\text{H}_2\text{N}_3^+$  cation<sup>20</sup> and dinuclear metal azide complexes.<sup>21</sup>

**Conclusions.** At low temperature, yellow  $[\text{Cs}][(\text{SO}_2)_2\text{N}_3]$  crystallizes from a solution of  $\text{CsN}_3$  in liquid  $\text{SO}_2$ . The crystal structure of  $[\text{Cs}][(\text{SO}_2)_2\text{N}_3]$  contains the  $(\text{SO}_2)_2\text{N}_3^-$  anion in which both  $\text{SO}_2$  ligands are coordinated to the same terminal nitrogen. This study provides the first crystal structure of a halide or pseudohalide anion bound to more than one  $\text{SO}_2$  ligand.

#### **Acknowledgements**

The authors thank the National Science Foundation, the Defense Advanced Projects Agency, and the Air Force Office of Scientific Research for financial support. M. G. thanks the Natural Sciences and Engineering Research Council of Canada for a postdoctoral fellowship, and R. H. , the Deutsche Forschungsgemeinschaft for a postdoctoral fellowship.

#### **Supporting Information Available**

Tables of structure determination summary, atomic coordinates, bond lengths and angles and anisotropic displacement parameters of  $[\text{Cs}][(\text{SO}_2)_2\text{N}_3]$  in CIF format. This material is available free of charge via the internet at <http://pubs.acs.org>.



## References

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Table 1. Crystal Data for [Cs][(SO<sub>2</sub>)<sub>2</sub>N<sub>3</sub>]

chemical formula	Cs N3 O4 S2
fw	303.06
T, K	130(2)
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)
<i>a</i> , Å	8.945(2)
<i>b</i> , Å	10.454(2)
<i>c</i> , Å	8.152(2)
β, deg	109.166(3)
<i>V</i> , Å <sup>3</sup>	720.0(2)
<i>Z</i>	4
ρ <sub>calc</sub> , g cm <sup>-3</sup>	2.796
μ, mm <sup>-1</sup>	5.685
<i>R</i> 1, <sup>a</sup> <i>wR</i> 2 <sup>b</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.0329, 0.0822
<i>R</i> 1, <sup>a</sup> <i>wR</i> 2 <sup>b</sup> (all data)	0.0333, 0.0826

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$$^a R1 = [\sum (F_o - F_c)/F_o]. \quad ^b wR2 = [\sum (w(F_o - F_c)^2)/\sum w(F_o^2)]^{1/2}.$$

Table 2. Experimental Bond Lengths [Å], Angles [°], and Contacts [Å] for [Cs][(SO<sub>2</sub>)<sub>2</sub>N<sub>3</sub>] and Calculated<sup>12</sup> Bond Lengths and Angles for the (SO<sub>2</sub>)<sub>2</sub>N<sub>3</sub><sup>-</sup> Anion

	obsd.	calcd.	
		B3LYP/6-31+G(d)	MP2/6-31+G(d)
N(2)-N(3)	1.141(6)	1.16	1.20
N(1)-N(2)	1.219(6)	1.21	1.23
S(1)-N(1)	2.201(5)	2.37	2.46
S(2)-N(1)	2.427(4)	2.40	2.48
S(1)-O(2)	1.449(4)	1.49	1.49
S(1)-O(1)	1.460(3)	1.48	1.49
S(2)-O(3)	1.433(4)	1.48	1.49
S(2)-O(4)	1.439(4)	1.48	1.49
N(1)-N(2)-N(3)	177.6(5)	178.9	177.5
S(1)-N(1)-S(2)	109.8(2)	117.5	100.7
N(2)-N(1)-S(1)	108.5(3)	108.7	102.3
N(2)-N(1)-S(2)	102.6(3)	112.9	99.3
O(2)-S(1)-O(1)	114.1(2)	115.2	116.3
O(3)-S(2)-O(4)	115.9(2)	115.5	116.3
O(2)-S(1)-N(1)	99.9(2)		
O(1)-S(1)-N(1)	97.1(2)		
O(3)-S(2)-N(1)	96.5(2)		
O(4)-S(2)-N(1)	96.3(2)		
obsd. contacts			
N(3)··Cs(1A)	3.377(4)	N(3)··Cs(1B)	3.434(4)
N(3)··Cs(1C)	3.548(4)	N(1)··Cs(1F)	3.351(4)
O(1)··Cs(1)	3.807(4)	O(1)··Cs(1D)	3.114(3)
O(2)··Cs(1)	3.287(3)	O(2)··Cs(1B)	3.139(3)
O(3)··Cs(1C)	3.176(3)	O(3)··Cs(1E)	3.430(3)
O(4)··Cs(1F)	3.243(4)	O(4)··Cs(1G)	3.329(3)

Table 3. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Cs}][(\text{SO}_2)_2\text{N}_3]$ .

	x	y	z	U(eq) <sup>a</sup>
Cs(1)	2061(1)	768(1)	8967(1)	18(1)
S(1)	5507(1)	2332(1)	7631(2)	17(1)
S(2)	7207(1)	5091(1)	10692(2)	18(1)
O(3)	8352(4)	4630(3)	12259(4)	24(1)
O(4)	7694(5)	6163(3)	9883(5)	28(1)
O(1)	4375(4)	3355(3)	7554(5)	25(1)
O(2)	5671(4)	1419(3)	9016(5)	24(1)
N(3)	9574(5)	2165(4)	10774(6)	26(1)
N(2)	8664(5)	2788(3)	9789(5)	20(1)
N(1)	7672(5)	3467(4)	8786(6)	25(1)

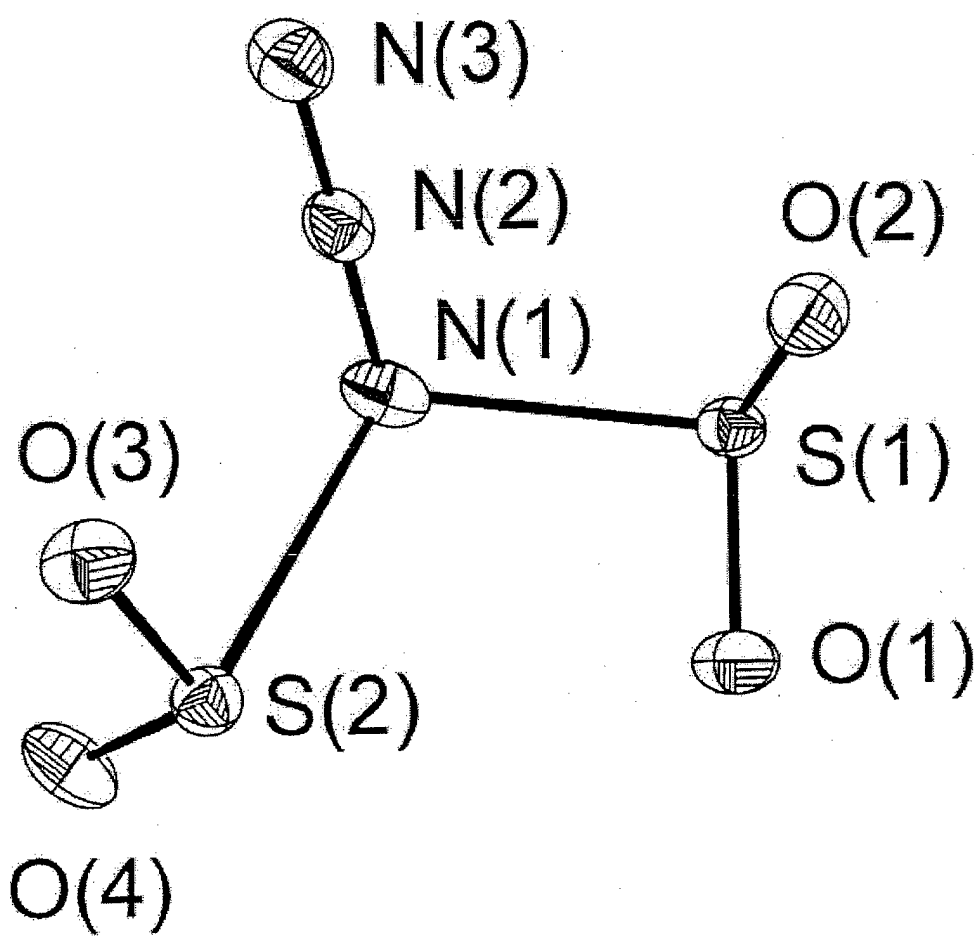
<sup>a</sup> U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

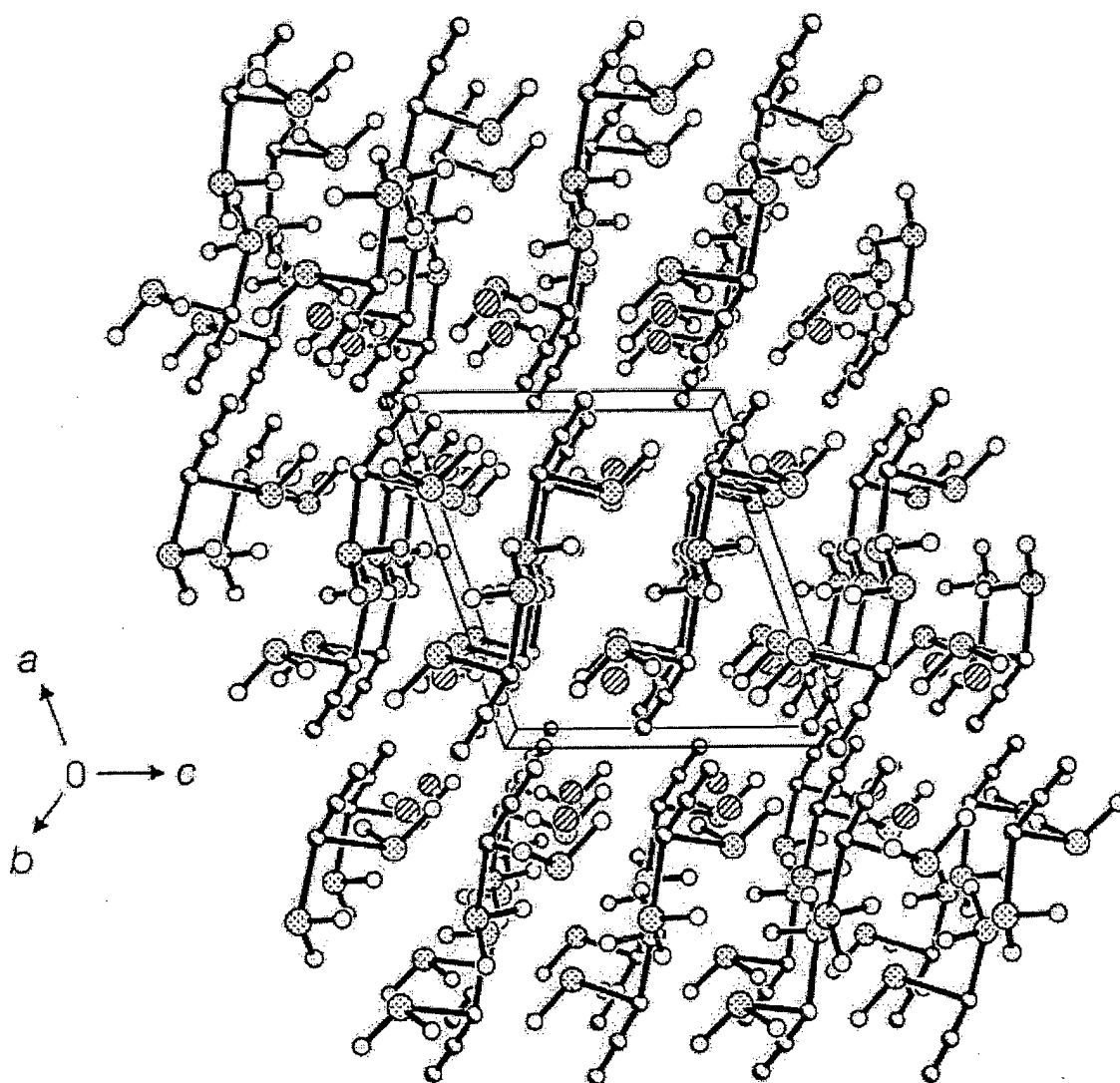
### Figure Captions

Figure 1. Structure of the  $(\text{SO}_2)_2\text{N}_3^-$  ion in  $[\text{Cs}][(\text{SO}_2)_2\text{N}_3]$ . Thermal ellipsoids are shown at the 50% probability level.

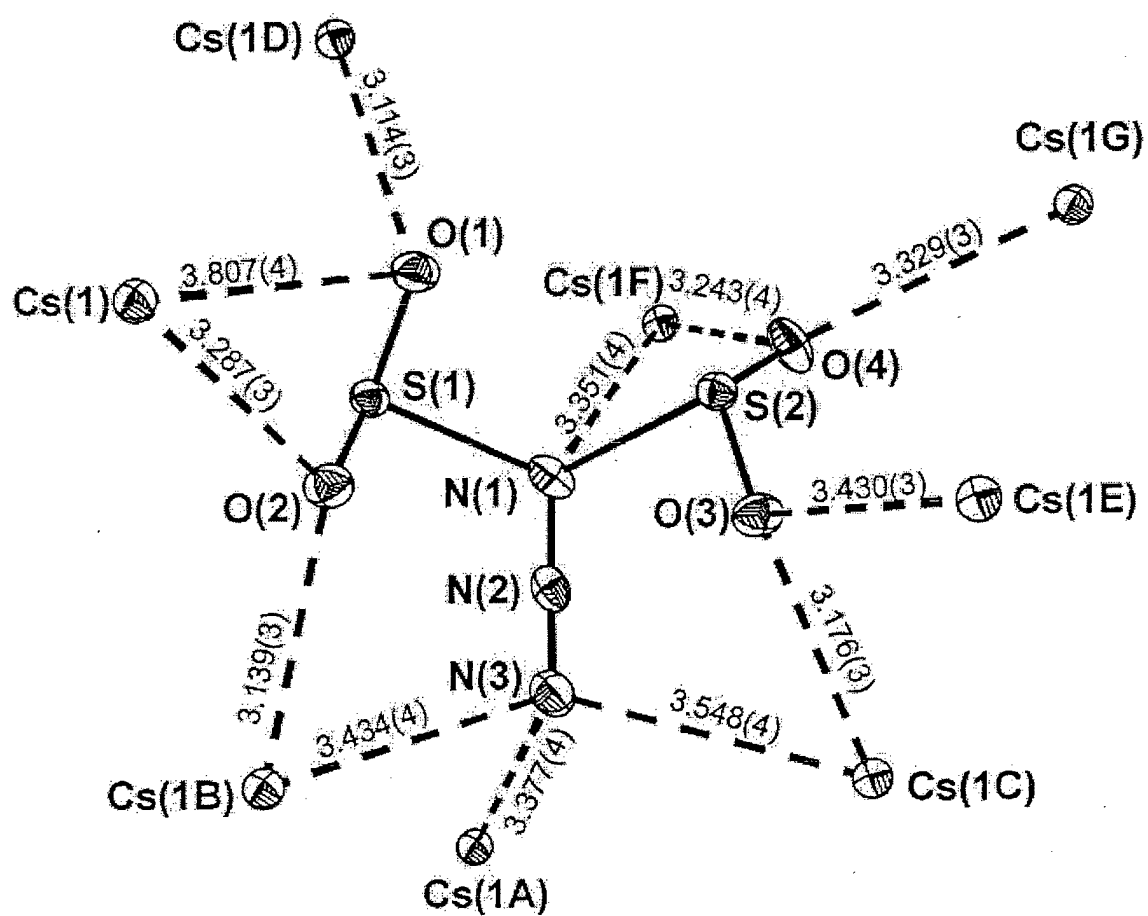
Figure 2. View of the packing of  $[\text{Cs}][(\text{SO}_2)_2\text{N}_3]$  along the  $b$ -axis.

Figure 3. Closest interionic contacts (Å) in  $[\text{Cs}][(\text{SO}_2)_2\text{N}_3]$ . Thermal ellipsoids are shown at the 50% probability level.









### The $(\text{SO}_2)_2\text{N}_3^-$ Anion

Karl O. Christe,\* Michael Gerken,  
Ralf Haiges, Stefan Schneider,  
Thorsten Schroer, Irena Tsyba,  
and Robert Bau

The recently reported 2:1 adduct between  $\text{SO}_2$  and the  $\text{N}_3^-$  anion,  $(\text{SO}_2)_2\text{N}_3^-$ , is structurally characterized by single crystal X-ray diffraction of the  $[\text{Cs}][(\text{SO}_2)_2\text{N}_3]$  salt. The crystal structure establishes the 1,1-coordination of two  $\text{SO}_2$  ligands to the  $\text{N}_3^-$  anion.

